



CHLORINE

GENERAL

Chlorine is a diatomic gas, which due to its high reactivity, is not found in its molecular form in nature. It forms approximately 0.15% of the Earth's crust mainly as sodium chloride in natural deposits and in sea water, and as carnallite ($\text{MgCl}_2\text{KCl}_6\text{H}_2\text{O}$) and sylvite (KCl).

Chlorine is a greenish-yellow gas or an amber liquid under high pressure or refrigeration. Chlorine gas has a pungent, irritating, suffocating odor. The odor threshold for chlorine in air has been reported to be 0.02-0.31 parts per million (ppm) for most individuals. It is slightly soluble in water and soluble in alkalis. Chlorine gas is 2½ times heavier than air.

PRODUCTION AND USE

Millions of tons of chlorine are commercially produced each year to meet the demands of the chemical industry and to purify domestic water supplies. The major processes for chlorine production are the electrolysis of sodium chloride brines via diaphragm or mercury cells.

The largest use of chlorine is in the manufacture of other chemicals, such as inorganic chlorides and chlorinated organic compounds. These chlorinated chemicals often find usage as solvents, anti-knock compounds, refrigerants, and pesticides. It is used in the production of plastics and resins. It is used by the pulp and paper industry for bleaching purposes. Chlorine is a powerful disinfectant and as such it is widely used in the chlorination of drinking water supplies, swimming pool water effluents, cooling system water, and sewage. Chlorine is also used in household bleaches, pharmaceuticals, and cosmetics, as well as in the beneficiating of ores and metal extraction.

HEALTH EFFECTS

Chlorine can adversely affect the body if it is inhaled or if it comes in contact with the eyes and skin. Molecular chlorine is a mucous membrane and respiratory system irritant. It has been reported that exposure of humans to 0.2 ppm for 4 to 20 minutes resulted in itching of the nose, while 1 ppm resulted in burning of the conjunctiva, scratchiness and dryness of the throat, coughing, and difficulty in inhaling. After 30 minutes exposure to 1.3 ppm, severe shortness of breath and violent headaches were noted. A concentration of 1,000 ppm was rapidly fatal after a few deep breaths. Both liquid and gaseous chlorine can produce ocular damage, and skin contact with the vapor or liquid may result in ulceration and necrosis. The LCLO (lowest lethal concentration) for man has been reported to be 430 ppm for 30 minutes exposure.

Severe acute effects from short-term, high level exposure have been documented from exposures of soldiers during World War I when chlorine was used as a war gas. Deaths were noted from bronchopneumonia, lobar pneumonia, purulent pleurisy, and tubercular meningitis. Disabilities occurred from bronchitis, pleurisy, tachycardia, nephritis, and dyspnea.

Severe, accidental exposures such as those occurring from the rupture of tank cars and cylinders have resulted in deaths and hospitalizations. Symptoms typically resulting from these brief, high concentration exposures were burning of the eyes with lacrimation, burning of the nose and mouth with rhinorrhea, coughing, choking sensation, and substernal pain. Nausea, vomiting, dizziness, and headache were also reported. Tracheobronchitis, pulmonary edema and pneumonitis were seen in those individuals who were hospitalized. Generally, respiratory distress and substernal pain subsided within 72 hours, while cough increased in frequency and severity, became productive, and disappeared after 14 days. Most case reports suggest that individuals recover completely and relatively rapidly after severe acute exposure. However, several follow-up studies have indicated that these severe acute exposures may result in pulmonary function abnormalities (declines in forced expiratory volume in one second or decreases in forced vital capacity) in individuals several years after the exposure occurred.

Several epidemiologic studies have attempted to relate industrial exposure to the frequency of pulmonary abnormalities and symptoms. The most extensive of these involved an in-depth study of 25 chlor-alkali plants in the United States and Canada. The study involved 332 male workers from diaphragm cell plants where time-weighted average (TWA) concentrations were known to range from 0.006 to 1.42 ppm. All but six individuals had TWA exposures below 1 ppm. Results of pulmonary function tests and chest X-rays revealed no evidence of permanent lung damage attributable to chlorine at the exposure levels reported. However, electrocardiograms from the exposed workers were abnormal for 9.4% versus 8.5% in controls. Anxiety and dizziness showed moderate correlation ($p=0.02$) with exposure, while leukocytosis ($p<0.05$) and lower hematocrit ($p<0.017$) exhibited some relation to chlorine exposure.

Chronic exposure of workers to concentrations in air around 5 ppm have been reported to result in erosion of tooth enamel.

Mutagenicity, Carcinogenicity, Teratogenicity

To date, there is no evidence that chlorine is mutagenic, carcinogenic, or teratogenic in humans.

Chemical changes have been observed in bacterial genetic material following treatment of these materials with chlorinating agents. It is also known that the action of chlorine on naturally occurring humic material has resulted in the formation of trihalomethanes in finished drinking water. Some of these trihalomethanes are mutagenic, and chloroform is a potential carcinogen.

When administered to female rats at high dose (100 ppm) in drinking water for a period of 2½ months prior to and throughout gestation, a slightly significant increase in percentage of total defects (skeletal and soft tissue) was reported. Fetal birth weights were also slightly decreased. However, no significant increases in percentage of total defects were noted in offspring of female rats dosed at levels of 1 ppm and 10 ppm. In other animal studies chlorine did not interfere with reproduction.

AQUATIC TOXICITY

Discharges of chlorine into waterways are fairly common because chlorine is used to disinfect effluents and to control fouling organisms in cooling system water. It is also widely used in the pulp and paper industries. When chlorine is added to fresh water, two forms of free chlorine, hypochlorous acid and hypochlorite ion, result. If ammonia is present, two forms of combined chlorine, monochloramine and dichloramine, also are formed. All four are quite toxic to aquatic organisms. Consequently, the term total residual chlorine (TRC) is used to refer to this sum of free chlorine plus combined chlorine when discussing freshwater aquatic toxicity. In saltwater, introduction of chlorine results in the formation of hypobromous acid, hypobromous ion, and bromamines. The term chlorine-produced oxidants (CPO) refers to the sum of these products when determining saltwater aquatic toxicity.

In general, the rate of lethality from TRC is rapid and the toxicity slope is steep. Freshwater fishes and invertebrates show a wide range of relative sensitivities to TRC. The LC₅₀ for a darter was 390 parts per billion (ppb), while for a stickleback the LC₅₀ was 710 ppb. But the acute values for two kinds of trout, two types of shiner, and a channel catfish were between 45 ppb and 90 ppb. Species mean acute toxicity values for a crayfish, stonefly, and amphipod were 266 ppb, 400 ppb, and 673 ppb, respectively, while those for two gastropods, two copepods and Daphnia magna ranged from 27 to 80 ppb.

For saltwater invertebrate species, adult blue crabs are relatively insensitive to CPO with the LC₅₀ ranging from 700 to 860 ppb. In sharp contrast, larvae of the eastern oyster and a copepod were very sensitive, with respective species mean acute values of 26 ppb and 29 ppb. Eleven species of saltwater fish had acute values ranging from 37 ppb to 270 ppb. The coho salmon, with a species mean acute value of 47 ppb, and the Atlantic silverside, with a species mean acute value of 37 ppb, were especially sensitive to CPO.

GUIDELINES AND STANDARDS

The National Institute for Occupational Safety and Health (NIOSH) has recommended a value of 0.5 ppm as a ceiling concentration to be measured over a period of 15 minutes. The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a threshold limit value (TLV) for chlorine in workplace air of 0.5 ppm as an 8-hour time-weighted average. Twenty-five ppm chlorine in air is considered by NIOSH to be immediately dangerous to life or health (IDLH). This IDLH concentration represents a maximum level from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects.

Chlorine is on the U.S. Environmental Protection Agency's (EPA) list of acutely toxic chemicals. EPA ambient aquatic life water quality criteria for chlorine have been adopted by the Virginia State Water Control Board as a water quality standard for chlorine in surface waters. According to this standard, the average daily concentration of total residual chlorine in freshwater shall not exceed 11 ppb and the average daily concentration of chlorine produced oxidant in saline waters shall not exceed 7.5 ppb. Furthermore, the one-hour average concentration of total residual chlorine in freshwater shall not exceed 19 ppb and the one-hour average concentration of chlorine produced oxidant in saline waters shall not exceed 13 ppb.

When there is a release of chlorine in an amount equal to or greater than its reportable CERCLA (Comprehensive Environmental Response Compensation and Liability Act) quantity of 10 pounds (4.54 kg), persons in charge of the facility or vessel are required to notify the National Response Center immediately. The toll free telephone number of the center is (800) 424-8802 and in the Washington metropolitan area is (202) 426-2675. The individuals should also notify the Virginia Department of Emergency Services at (804) 323-2300.

FIRE, EXPLOSION AND REACTIVITY POTENTIAL

Neither liquid nor gaseous chlorine is flammable or explosive, but most combustible materials will burn in gaseous chlorine as they do in oxygen. Also, chlorine is a powerful oxidizing agent and is very active chemically with many other materials. Chlorine, therefore, will

form flammable and/or explosive mixtures/compounds with many common chemicals, especially acetylene, turpentine, ether, ammonia, hydrogen, hydrocarbons, many metals, hot or moist steel, gasoline and petroleum products, fuel gas, sulfur, fluorine, and ethylene. Chlorine should be separated from these chemicals, as well as from combustible organic and easily oxidized materials. Elevated temperatures may cause chlorine containers to burst.

Materials which come into contact with liquid or gaseous chlorine must be carefully selected to avoid excessive corrosion or more serious events. No attempt should be made to handle or store chlorine without reviewing the Chlorine Institute's (New York) manual.

FIRST AID

For inhalation exposures move the victim to fresh air. Make sure rescuers are wearing self-contained breathing apparatus and protective clothing. If victim is not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call for emergency medical care. A severe inhalation should be hospitalized and treated as a respiratory emergency. Chlorine inhalation in an individual with compromised pulmonary function should be regarded as a severe inhalation and thus as a respiratory emergency. The victim should be monitored for respiratory function for 24 hours to assure that pulmonary edema does not develop.

In case of eye contamination with liquid chlorine or high concentrations of chlorine gas, provide immediate and continuous irrigation with flowing water for at least 30 minutes. Prompt medical consultation is necessary.

In case of skin contamination with liquid chlorine or high concentrations of chlorine gas, provide immediate flushing via flowing water or shower for at least 15 minutes. Contaminated clothing and shoes should be removed at the site. If irritation is present after washing, get medical attention.

SPILLS AND EMERGENCIES

In the case of a spill or emergency immediately notify appropriate authorities (see section on "Guidelines and Standards"), and provide for first aid. Isolate the hazard area and allow entry only of qualified individuals wearing appropriate personal protective equipment (positive pressure self-contained breathing apparatus and full protective clothing). Ventilate the area of the spill or leak, if appropriate. Keep upwind of the spill. Since chlorine is heavier than air, keep out of low areas. Keep combustibles away from the spill area. Stop the leak, if you can do so without risk. Emergency leak kits are available and the Chlorine Institute can provide information about these. If possible, leaking containers should be placed in such a position that only gas and not liquid can escape, since the volume of gaseous chlorine formed by vaporization of liquid chlorine is about 450 times its original liquid volume. Do not use water directly on a chlorine leak or spill area. A fog nozzle may be used in the area to absorb chlorine gas. Water may be used on containers that are not leaking in order to keep them cool during a fire. Isolate area until gas has dispersed. If water pollution occurs, notify the Virginia State Water Control Board.

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